

PATENT SPECIFICATION

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(54) SELECTIVE PLATING OF PLASTICS MOULDINGS

(71) We, BAKELITE XYLONITE LIMITED, a British Company, of 27 Blandford Street, London, W.1., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the metal-plating of moulded plastics articles, and provides a process for selectively metalplating plastics mouldings.

It has been proposed to metal-plate certain plastics materials by the processes of electroless- and electro-plating. When it is desired to selectively plate the surface of the plastics article it has hitherto been necessary, when the moulding is made of a plateable material, to stop-off selected areas of the surface by spraying or brushing a stop-off lacquer on the areas on which plating is not wanted. Alternatively the moulding may be made of a plastics material that is resistant to the plating process used in which case the surface where plating is desired is modified by the selective application of an adhesion lacquer.

Both these above methods rely on careful application of the lacquer or lacquers, and clearly defined boundaries between the plated and non-plated areas are difficult to achieve.

The present invention provides a process for the manufacture of a selectively metal-plated plastics moulding, which comprises forming an article by a 2-shot injection or compression-moulding process using a plateable plastics material and an unplateable plastics material, the arrangement of the mould and the order of the shots being such that those portions of the composite article which it is desired to plate are formed of the plateable plastics material, and subjecting the article to a plating process.

The term "2-shot injection- or compression-moulding" used in this specification includes 3-shot and multi-shot moulding processes.

The term "plating process" used in this specification means electroless- and/or electro-plating process.

The term "plateable plastics material" in [Price 25p]

this specification means any modified or unmodified plastics material which can be plated by a given electroless- or electro-plating technique. Similarly the term "unplateable plastics material" means any modified or unmodified plastics material which cannot be plated by the same electroless- or electro-plating technique.

By "modified plastics material" there is meant any normally non-plateable plastics material that has been rendered plateable during or after its manufacture by any means, for example by application or incorporation of an etchable compound, or any normally plateable plastics material that has been rendered non-plateable during or after its manufacture of an etch resisting compound. A polybutadiene rubber incorporated in polypropylene, for example, may render the latter plateable; alternatively p.v.c. for example, incorporated into an A.B.S. copolymer may render the latter non-plateable.

The process of the invention is especially suited for the manufacture of integral mouldings comprising two or more unplated areas that differ from one another in some of their physical characteristics, for example their colour, and one or more metal-plated areas. For example, there may be produced a motor car rear light lens, consisting of clear, red and amber areas surrounded by a metal-plated border.

When employing injection-moulding techniques it is advantageous to use an injection-moulding apparatus that enables shots of different materials to be introduced into different parts of the mould. The injection-moulding apparatus may comprise at least two injection cylinders and means of transferring the mould from the cylinder containing non-plateable material to the cylinder containing plateable material or *vice versa*. This may be done automatically or semi-automatically. Alternatively, a standard single cylinder injection machine may be used firstly to produce inserts and then to mould the second material around them. The mould may have a cavity A for producing the inserts and a separate cavity B for moulding around them. For the first run, cavity B is stopped off at a convenient

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point in the runner system. For the second run, the runner is open to cavity B and closed to cavity A. Alternatively, a single cavity mould may be used. For the first run the cavity is fitted with a metal insert occupying the space to be filled with the second material. This metal insert is removed for the second run and a plastic insert placed in the cavity for each shot.

The order of the shots in either an injection- or compression-moulding process may be governed by the relative softening points of the materials. For example, when a moulding produced by a shot of a relatively low-softening plastics material would be distorted by a subsequent shot of a higher-softening plastics material it is advantageous to reverse the order of those two shots. In addition, the order of shots may be governed by the flexibility and/or the shrink characteristics of the plastics material employed, it being necessary to achieve a seal, between the various components, against ingress of etchants and plating media, also against deleterious weather conditions subsequent to plating while also avoiding distortion of one or other of the components. When rigid materials are employed throughout, it is advantageous to mould the peripheral material of a composite moulding secondly so that the shrinkage forces set-up on cooling tend to produce a shrink-fit of the peripheral portion of the moulding on to the insert. On the other hand, if a flexible material is employed for the insert portion of the composite moulding, it is advantageous to mould this insert portion secondly to avoid distortion and to achieve the seal by moulding or cutting a recess along or close to the inner edge of the firstly produced peripheral portion to provide a key for the second shot. Shrinkage of the second shot produces tensile forces causing a shrink fit at the interfaces or join.

In a modification of the process of the invention, the portion of the final moulding which it is desired to plate is moulded in a first stage from a normally non-plateable plastics material, and the first stage moulding is treated to render the material plateable, for example, by application of an A.B.S. adhesion lacquer. The treated moulding is then used as

an insert in a subsequent second-shot moulding and the composite moulded article is then plated, the plating being selective to the treated portion(s) of the moulded article.

The mouldings may be prepared from thermoplastic or thermosetting materials, the only criterion governing the choice of materials and the plating process being that the non-plateable material must not be deleteriously attacked by the solutions used in the plating process.

Two methods of applying an electroless metal coating are preferred.

In the first of these the surface of the moulding is etched and then activated by immersion in a suspension of colloidal palladium and after rinsing it is immersed in an accelerator which dissolves or coagulates any protective colloid present. In the second, the activating step is comprised by immersing the moulding in a solution of a palladium salt and after rinsing, the moulding is immersed in an accelerator comprising a solution of a reducing agent.

Thus in a commercial process which has the description "Macuplex RT" ("Macuplex" is a Registered Trade Mark of Electro-Chemical Engineering Co. Ltd.) the following steps are involved:

- a) Immerse in "Macuplex" Etchant XL 55 or XL 43, which are based on chromic acid.
- b) Rinse in clean water.
- c) Immerse in "Macuplex" Activator XD 34 which is a palladium suspension.
- d) Rinse in clean water.
- e) Immerse in "Macuplex" Accelerator XD 45.
- f) Rinse in clean water.
- g) Immerse in "Macuplex" Electroless Nickel 9340 solution, which contains a nickel salt and a reducing agent.

The second method involving the use of a hypophosphite as reducing agent can be operated in the following way:

- a) Immerse in an aqueous etch solution for up to six minutes at 65°C, having the following composition range:

Chromium trioxide	10 to 25% W/W	} 40% W/W min.
H ₂ SO ₄ (Conc.)	25 to 35% W/W	

- b) Rinse in clean water.
 - c) Immerse in an activator solution for three minutes at 50°C having a composition of:

0.1—20gm/litre Pd Cl ₂ and 1—20 mls/litre conc. HCl.	
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 - d) Rinse in clean water.
 - e) Immerse for at least one minute, at 25°C in an aqueous accelerator solution containing 5 to 100 gm/litre sodium hypophosphite.
 - f) Rinse in clean water.
 - g) Immerse for five to ten minutes at 30°C in an aqueous electroless nickel solution having a composition:

Nickel chloride	10 to 100 gm/litre
Ammonium chloride	25 to 100 gm/litre
Sodium hypophosphite	5 to 50 gm/litre
Sodium citrate	50 to 200 gm/litre

 the pH of which is controlled to between 8 to 10.
- If desired the two methods may be com-

bined and the etch from the second process may precede the other steps of the "Macuplex" process.

5 The most suitable plastics material for use as the plateable material is a known copolymer or graft-copolymer of acrylonitrile, butadiene and styrene (A.B.S.), the percentages of the components being within the ranges 16 to 40%, 15 to 40% and 20 to 60% respectively. Other polymerized monomers may be present either discretely or copolymerized with out or more of the components of the A.B.S. copolymer. Examples of suitable A.B.S. materials are "Cycolac" EP 3510 and 15 Novadur P 20 M. ("Cycolac" is a Registered Trade Mark of Marbon Chemicals Division of Borg Warner Corp. and Novadur is a trade name of Farbenfabriken Bayer A.G.).

20 As materials that normally are not plateable by the preferred plating processes and are not deleteriously affected by the solutions used therein there may be mentioned the following unmodified plastics materials: plasticized or unplasticized polymers or copolymers of vinyl 25 chloride, propylene, 4 - methylpentene -1, styrene including styrene/acrylonitrile copolymers, low-density polyethylene and polycarbonates. Mouldings made from crystal polystyrene, styrene/acrylonitrile copolymers 30 or polycarbonates with A.B.S. by a 2-shot process are very well suited to being selectively plated by the process of the invention.

35 Other unmodified plastics materials that are envisaged as being not deleteriously affected by the plating solution used in the preferred process or slight modifications thereof are high-density polyethylene, polysulphones, and polyphenylene oxide.

40 Stressed articles made from certain toughened polystyrenes or polymers or copolymers of acrylic or methacrylic acid esters, especially polymers or copolymers of methylmethacrylate as produced by injection moulding as non-plateable plastics material are unsatisfactory for use in the process when the 45 plating solutions are as described hereinbefore since these plastics materials are affected by

the solutions used in the plating process. The surface of stressed articles from polymethylmethacrylate, for example, is attacked during 50 the preliminary etching step and also may become discoloured due to treatment with the accelerator. Some slight modification of the plating process is therefore necessary when 55 these latter materials are to be used in the process of the invention. Low stressed mouldings from these polymers can be used satisfactorily if the periods of the etching and acceleration steps are reduced. In this case it is desirable that the plateable part of the 60 article is also of substantially unstressed material as the bond strength of the plating is then improved. Unstressed or low stressed mouldings can, of course, be obtained by regulating the moulding conditions, for example, 65 by using a very low filling rate or by altering the surface characteristics of the mould.

It will be appreciated that certain plastics that are plateable by one plating process may not be plateable by another and *vice versa* 70 and the description of a material as "plateable" or "non-plateable" must be read in the context of the particular plating process that is to be applied. The references hereinbefore to specific materials as being plateable or 75 non-plateable may therefore apply only to the two specific plating processes described and it may, for example, be possible by using a more drastic etch to plate certain of the materials stated to be unplateable. 80

The invention is illustrated by the following Examples. The words "Macuplex" and "Cycolac" are Registered Trade Marks.

EXAMPLE 1

85 A moulded article was produced by a 2-shot injection moulding process. A disc of crystal polystyrene was formed in a first shot, and the disc was used as an insert in a second mould into which a second shot comprising an ABS copolymer was injected. 90

The moulding was then electroplated by the "Macuplex R.T." process as set out in the following Table:

TABLE

Solution	Function	Conditions
XL 43	Etching solution	6 mins. at 70°C, followed by a water rinse
XD 34	Activator	3 mins. at 30°C. followed by a water runse
XD 45	Accelerator	1½ mins. at 45—50°C. followed by a water rinse
Electroless Ni 9340	Forms conductive surface layer	6 mins. at 30°C followed by a water rinse
Strike bath Bright Ni		5 mins. at 30 amps/sq. ft.
Cupralgo 6 Bright acid Cu		20 mins. at 40 amps/ sq. ft.
Efco 66 Bright Ni bath		10 mins. at 40 amps/sq. ft.
Chromylite K 50		3 mins. at 120 amps/sq. ft.

- 5 The finished plated article had a transparent centre disc surrounded by a bright electroplated rim. The junction between the plated and non-plated areas was clear and well defined, and there was no visible etching of the unplated transparent portion.

EXAMPLE 2

- 10 Composite disc mouldings were made having centres made from varying materials and rims made from an acrylonitrile/butadiene/styrene copolymer Cycolac EP 3510. For each disc the centre portion was first moulded and this was used as an insert in a further operation in which a ring of ABS copolymer was moulded round it. The ABS copolymer was moulded at a very low injection rate so that a substantially stress-free moulding was obtained.

- 20 The centres of the discs were made from commercial grades of polystyrene, styrene/acrylonitrile copolymer, polycarbonate, poly-4-methyl-pentene-1, polypropylene and substantially stress-free polymethymethacrylate.

- 25 The discs were plated using the following system.

Etch

- 30 Made up of chromium trioxide, sulphuric acid and water in the following proportions:—

Chromium trioxide	20% W/W
Sulphuric acid (Conc)	30% W/W
Water	50% W/W

Activator

A colloid of palladium in stannous chloride hydrochloric acid mixture comprising:

Palladium chloride	0.3 gm
Stannous chloride	10.0 gm
Hydrochloric acid (conc.)	300 mls
Water	to 1 litre

Accelerator

An aqueous solution of 0.004 gm/litre of palladium chloride in dilute HCl at pH 4.

Electroless Nickel

Solution as follows:

Nickel chloride	60 gm
Ammonium chloride	40 gm
Sodium hypophosphite	30 gm
Sodium citrate	80 gm
Water	to 1 litre

pH controlled between 8 to 10.

Electrolytic Section

Standard metal plating line incorporating electroplating baths containing the following proprietary solutions:

- "Cupraglow" 6 Cruickshanks Division of Forestal Industries (U.K.) Ltd. specification.
- "Efco" 66 marketed by Electro-Chemical Engineering Co. Ltd.
- "Chromylite" K 50 marketed by Electro-Chemical Engineering Co. Ltd.

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Plating Method

The samples were all plated using a one jig system incorporating the following stages:

e) Rinsed in Chrome Neutralizer as supplied by W. Cannings & Co. Ltd. 45

- 5 1) *Cleaning*
Dipped in alkaline Minco solution, as marketed by W. Canning & Co. Ltd., maintained at 60°C, to remove dirt and grease.
Thoroughly rinsed in agitated water.
- 10 2) *Etch*
Immersed in etch for 6 minutes at a bath temperature of 65°C.
Air agitation provided.
Thoroughly rinsed in agitated water.
- 15 3) *Activator*
Immersed for 4 minutes at a bath temperature of 70°C. Thoroughly rinsed in agitated water.
- 20 4) *Accelerator*
Immersed for 45 seconds at a bath temperature of 49°C. Thoroughly rinsed in agitated water.
- 25 5) *Electroless Nickel*
Immersed for 7 minutes at a bath temperature of 30°C. Thoroughly rinsed in agitated water.
- 30 6) *Electroplating*
 - a) Immersed in electroplating bath (i) above containing bright acid copper solution "Cupraglow" 6 5 minutes at 30 amps/sq. ft. followed by 25 minutes at 40 amps/sq. ft. to deposit 0.001 in. copper.
 - 35 b) Immersed in electroplating bath (ii) above containing "Efco" 66 for 16 minutes at 40 amp/sq. ft. to deposit 0.0004 in. bright nickel.
 - 40 c) Immersed in electroplating bath (iii) above containing "Chromylite" K 50 for 3 minutes at 120 amps/sq. ft. to deposit 0.00001 in. bright chrome.
 - d) Thoroughly rinsed in agitated water.

This method produced satisfactory platings on all the discs except that which had a polymethylmethacrylate centre, in which case the centre was badly attacked by the various solutions. 50

A satisfactory selectively-plated article was obtained with this disc when the etch time was reduced to 2 minutes and the accelerator treatment time was reduced to 10 seconds. 55

EXAMPLE 3

Three ABS/polymethylmethacrylate composite mouldings were prepared and plated as described in Example 2 employing the reduced etch and accelerator times. 60

The plated mouldings were subjected to a test involving ten thermal cycles. Each cycle involved maintaining the mouldings at -20°F for a period of one hour followed by maintaining them at 190°F for one hour. After 10 cycles had been applied, it was found that no blistering of the plating had occurred. In addition, stripping tests showed that no diminution of adhesion between the mouldings and plating had occurred. 65

The unplated portions of the mouldings were not visibly affected. 70

EXAMPLE 4

Example 2 was repeated using the following plating system: 75

Etch

Chromium trioxide	25% W/W	
Sulphuric acid (conc.)	30% W/W	
Water	45% W/W	80

Activator

Palladium chloride	15 gm
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Hydrochloric acid (conc.) } to 1 litre
Water } at pH 3.5

Accelerator

85 Sodium hypophosphite	70 gm
Water	to 1 litre

Electroless Nickel and Electrolytic Section
As in Example 2.

Plating Method

- 90 1) *Cleaning*
The samples were cleaned as in Example 2 and thoroughly rinsed in agitated water.
- 95 2) *Etch*
Immersed in etch for five minutes at bath temperature of 65°C.
Air agitation provided.

Thoroughly rinsed in agitated water.

- 3) *Activator*
Immersed for three minutes at bath temperature of 50°C. 100

Thoroughly rinsed in agitated water.

- 4) *Accelerator*
Immersed for 90 seconds at bath temperature of 25°C. Thoroughly rinsed in agitated water. 105

- 5) *Electroless Nickel*
Immersed for seven minutes at bath temperature of 30°C.
Thoroughly rinsed in agitated water. 110

- 6) *Electroplating*
As in Example 2.
All the discs were satisfactorily selectively

plated except that having the polymethylmethacrylate centre. Satisfactory selective plating was obtained with this disc when the etch time was reduced to two minutes and the accelerator treatment time was reduced to 10 seconds.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a selectively metal-plated plastics moulding which comprises forming an article by a 2-shot injection or compression-moulding (as hereinbefore defined) process using a plateable plastics material (as hereinbefore defined) and an unplateable plastics material (as hereinbefore defined), the arrangement of the mould and the order of the shots being such that those portions of the composite article which it is desired to plate are formed of the plateable plastics material, and subjecting the article to a plating process.

2. A process as claimed in claim 1 wherein an electroless plated metal coating is applied to the article by a method which involves the steps of

- a) treating the article with an etchant;
- b) treating the article to catalyse the deposition of metal on to the article with an activator and an accelerator; and
- c) treating the article with an electroless plating solution.

3. A process as claimed in claim 2, wherein the etchant is based on chromic acid.

4. A process as claimed in claim 2 or claim 3, wherein the activator is a suspension of colloidal palladium and the accelerator is such that it dissolves or coagulates any protective colloid present.

5. A process as claimed in claim 4, wherein the activator is an aqueous mixture of colloidal palladium, stannous chloride and hydrochloric acid and the accelerator is an aqueous solution of palladium chloride and hydrochloric acid.

6. A process as claimed in claim 2 or claim

3, wherein the activator is a solution of a palladium salt and the accelerator is a solution of a reducing agent.

7. A process as claimed in claim 6, wherein the activator is an aqueous solution of palladium chloride and hydrochloric acid and sodium hypophosphite.

8. A process as claimed in any one of claims 2 to 7, wherein the electroless plating solution contains a nickel salt and a reducing agent.

9. A process as claimed in any one of claims 2 to 8, wherein the plateable plastics material is a copolymer or graft copolymer of acrylonitrile, butadiene and styrene as hereinbefore defined.

10. A process as claimed in any one of claims 2 to 9, wherein the non-plateable material is a plasticized or unplasticized polymer or copolymer of vinyl chloride, propylene, 4-methyl-pentene-1, styrene including a styrene/acrylonitrile copolymer, low-density polyethylene or polycarbonate.

11. A process as claimed in any one of claims 2 to 9, wherein the non-plateable material is a toughened polystyrene or a polymer or copolymer of an acrylic acid ester or of a methacrylic acid ester and the article is so moulded that the stresses therein are reduced to a minimum.

12. A process as claimed in claim 2, wherein the electroless plating process is substantially as described herein.

13. A process as claimed in claim 1, conducted substantially as described in any one of the Examples herein.

14. Selectively metal plated plastics mouldings whenever obtained by a process as claimed in any one of claims 1 to 13.

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